THE DETERMINATION OF THE COMPOSITION OF MnO_2—Mn_2O_3—Mn_3O_4—$H_4BaMnMn_8O_{20}$ SYSTEMS

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In several papers *Gy. Grasselly* [1, 2] and *Gy. Grasselly* and *E. Klivényi* [3, 4, 5] deal with the thermal properties of the manganese oxides of higher valency as well as with the determination of the composition of mixtures containing various manganese oxides on the basis of their thermal behaviour. The examinations were first carried out with well defined pure artificial substances, or with their mixtures of known composition. Concerning natural substances first of all the composition of Hungarian sedimentary manganese oxide ore minerals were treated. The examination of the composition of these minerals show that the presence of pyrolusite, manganite and psilomelane must be taken into account. Accordingly the method for the estimation of the composition of the system of the MnO_2—Mn_2O_3—Mn_3O_4 components elaborated by *Gy. Grasselly* was modified and supplemented respectively, so that in addition on the pyrolusite (MnO_2) and manganite ($Mn_2O_3 \cdot H_2O$) components instead of hausmannite (Mn_3O_4) psilomelane ($H_4BaMnMn_8O_{20}$) was taken into account. Thus knowing the thermal properties of psilomelane a method enabling the determination of the mineral composition in the presence of these three components was elaborated.

In the present paper this method — extended to the determination of systems containing four components MnO_2, Mn_2O_3, Mn_3O_4 and natural original psilomelane *(Rudabánya)* and their mixtures of known composition. The determination was similarly to the previously mentioned ones carried out on the basis of the thermal properties of the single components. The experimental part and practical realization is in complete agreement with the method described in the papers referred to and will not be dealt with in detail here.

At the determination of the composition of the system containing four components knowing the thermal properties of the single components the consideration was taken into account that of the four components involved after ignition in air for 3 hours at 600 °C a difference in the grade of oxidation could only be observed in the case of MnO_2 and Mn_3O_4, inasmuch as the first transforms by giving off and the second by taking up oxygen into Mn_2O_3, whereas the Mn_2O_3 and psilomelane components remain unchanged. In a nitrogen current on the action of ignition for three hours at 600 °C only MnO_2 gives off oxygen and transforms into Mn_2O_3 — hence shows the same change as at ignition in air at 600 °C — whereas the other components remain unchanged. On this basis the total MnO content of the system containing four components, the active oxigen content and the changes of the active oxigen content due to the effect of the different ignitions give with the application of a suitable method of calculation the original composition of the system — in the case of natural substances the mineral composition of the system — quantitatively.

For the determination of the composition the method of *Grasselly* [1, 2] plots in the case of three components (MnO_2, Mn_2O_3, Mn_3O_4) graphically on a triangular diagram the point giving the percentual quantity of the various components. However, in the case of four components the method of plotting using a triangular diagram cannot be applied. Considering that the plotting of a system containing four components on a diagram in the plane is fairly complicated, for the sake of simplicity the following solution was chosen.

The system containing four components — after having completed the necessary examinations — is reduced by direct calculation of the quantity of two components into two components and the appropriate values of the system containing two components are plotted on a diagram.

The data needed for the quantitative determination are: the total MnO and active O content of the system at 20 °C (room temperature), at 600—650 °C after igniting for three hours and that of a separate sample after igniting it for three hours in a nitrogen current. In all the examinations the MnO and O values were recalculated to 100 per cent.

The process of the determination is as follows:

1. The first step is to determine the amount of MnO_2. The difference between the active oxygen content measured at 20 °C and after igniting in a nitrogen current at 600 °C is proportional with the amount of MnO_2. (Namely in the course of this ignition of the four possible components anly MnO_2 transforms by giving off oxygen into Mn_2O_3, the other three components remain unchangend.) If the oxygen change which takes place at the transformation of the pure ideal MnO_2 into Mn_2O_3 is known on the basis of the measured oxygen change, the ΔO, the quantity of MnO_2 may be calculated.

The tables contained in the appendix make this recalculation easier as they illustrate in the case of all four components pro per cents the MnO and active O content furthermore, in that of the MnO_2 and Mn_3O_4 components the oxygen change, the $\pm \Delta O$ too. The difference between the two active oxigen values obtained previously — visible on the table of MnO_2 — the amount of the O_2 in per cents to which it corresponds, the amount of MnO and active O belonging to the quantity of MnO_2 expressed in per cents must be taken into account.

2. The second step is the determination of the quantity of Mn_3O_4, Considering that MnO_2 shows the same change if it is ignited in air or in a nitrogen current, if a difference can be observed in the active O content of the sample after it has been ignited in air or in a nitrogen current, this difference can only be due to the transformation of Mn_3O_4 into Mn_2O_3. Hence, this difference is proportional with the amount of Mn_3O_4. The difference between the two values is the ΔO belonging to the amount of Mn_3O_4. This value is visible on the table of Mn_3O_4 it can be seen to how many per cents of Mn_3O_4 this corresponds furthermore, how much MnO and O belongs to this percentual value.

3. The MnO and O content, respectively, obtained in the case of MnO_2 and Mn_3O_4 is added. These values are subtracted from the MnO and active O values obtained from the original sample determined at 20 °C. The residual MnO and O content belongs either to one of the remaining two components as a third one — and then only three components were present — or is divided between the two components.

4. If the system only contained three components then the MnO and O content remaining after the substraction merely defines a certain amount of the percentage. Thus, on the tables of Mn_2O_3 and psilomelane it can be seen whether the obtained MnO and O value belong together. If it seems that the amount of the obtained MnO in the tables does not belong to the active O value found by us then the common presence of the two components must be taken into account.

5. If the MnO and O values are only distributed between two components then the given MnO and O values belong only to *one* given composition. This composition is obtained by recalculating to 100 per cent the MnO and O content now already belonging to a system with two components. The values obtained in this manner are plotted on a diagram on the perpendicular axis of which on one side the MnO and O content of the Mn_2O_3 and on the other that of the psilomelane may be measured.

The one end point of the horizontal axis represents hence 100 per cent Mn_2O_3, the other end point 100 per cent psilomelane. The dots denoting MnO and O respectively are connected. The obtained MnO and O values are plotted on the corresponding lines of the diagram (the MnO and O values must be situated under each other) and the dots obtained in this manner plotted onto the absciss give the composition of the reduced system containing two components. In view of the fact that the amount of Mn_2O_3 and psilomelane was previously calculated to 100 per cent this percentage amount must be reduced to that percentage ratio with which the two oxides were represented in the system containing four components.

6. Finally we control on the corresponding tables whether the values recorded on the diagram and subsequently recalculated are correct, i. e. whether the total amount of the four components gives the

100 per cent, as well as if the sum furnished by the obtained MnO and O values is in agreement with the MnO and active O content of the original sample determined at 20 °C.

The determination of the composition was carried out in the presence of four components of artificial and natural manganese oxides with known composition. (A natural mineral association in which all the four components would have been present was not examined.)

REFERENCES

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3. Grasselly, Gy., Klivényi, E.: Concerning the Thermal Properties of the Manganese Oxides of Higher Valencies. Acta Min. Petr. Tom. IX.
4. Grasselly, Gy., Klivényi, E.: On the Stability of Mn_3O_4. Acta Min. Petr. Tom. IX.
5. Grasselly, Gy., Klivényi, E.: Method for the Determination of the Mineral Composition of Sedimentary Manganese Oxide Ores on the Basis of their Thermal Properties. Acta Min. Petr. Tom. X.

APPENDIX

In the tables of the appendix are summed up the data of MnO_2, Mn_2O_3, Mn_3O_4 and $H_4BaMnMn_8O_{20}$ referring to each per cent. The summary referring to each per cent does not mean, that the determination is not possible with a greater accuracy. Of course the corresponding data are calculable to each tenth of a per cent too these data, however, are not included in these tables.

The notation of the tables are the follows:

% = the total quantity of the single oxides in per cent

MnO = MnO contant of the oxides referring to their percentage content

»O« = active oxigen content of the oxides referring to their percentage content

ΔO = the change in the »O« content pro per cent of each oxides, when the corresponding oxide fully transforms into Mn_2O_3. This change is by MnO_2 negative, by Mn_3O_4 positive.

MnO_2

%	MnO	»O«	$\pm \Delta$ O	%	MnO	»O«	$\pm \Delta$ O
1	0,81	0,18	0,08	51	41,61	9,38	4,21
2	1,63	0,36	0,16	52	42,43	9,56	4,30
3	2,44	0,55	0,24	53	43,24	9,75	4,38
4	3,26	0,73	0,33	54	44,06	9,93	4,46
5	4,08	0,92	0,41	55	44,88	10,12	4,54
6	4,89	1,10	0,49	56	45,69	10,30	4,63
7	5,71	1,28	0,57	57	46,51	10,48	4,71
8	6,52	1,47	0,66	58	47,32	10,67	4,79
9	7,34	1,65	0,74	59	48,14	10,85	4,87
10	8,16	1,84	0,82	60	48,96	11,04	4,96
11	8,97	2,02	0,90	61	49,77	11,22	5,04
12	9,79	2,20	0,99	62	50,59	11,40	5,12
13	10,60	2,39	1,07	63	51,40	11,59	5,21
14	11,42	2,57	1,15	64	52,22	11,77	5,29
15	12,24	2,76	1,24	65	53,04	11,96	5,37
16	13,05	2,94	1,32	66	53,85	12,14	5,45
17	13,87	3,12	1,40	67	54,67	12,32	5,54
18	14,68	3,31	1,48	68	55,48	12,51	5,62
19	15,50	3,49	1,57	69	56,30	12,69	5,70
20	16,32	3,68	1,65	70	57,12	12,88	5,78
21	17,13	3,86	1,73	71	57,93	13,06	5,87
22	17,95	4,04	1,81	72	58,75	13,24	5,95
23	18,76	4,23	1,90	73	59,56	13,43	6,03
24	19,58	4,41	1,98	74	60,38	13,61	6,11
25	20,40	4,60	2,06	75	61,20	13,80	6,20
26	21,21	4,78	2,15	76	62,01	13,98	6,28
27	22,03	4,96	2,23	77	62,83	14,16	6,36
28	22,84	5,15	2,31	78	63,64	14,35	6,45
29	23,66	5,33	2,39	79	64,46	14,53	6,53
30	24,48	5,52	2,48	80	65,28	14,72	6,61
31	25,29	5,70	2,56	81	66,09	14,90	6,69
32	26,11	5,88	2,64	82	66,91	15,08	6,78
33	26,92	6,07	2,72	83	67,72	15,27	6,86
34	27,74	6,25	2,81	84	68,54	15,45	6,94
35	28,56	6,44	2,89	85	69,36	15,64	7,02
36	29,37	6,62	2,97	86	70,17	15,82	7,11
37	30,19	6,80	3,05	87	70,99	16,00	7,19
38	31,00	6,99	3,14	88	71,80	16,19	7,27
39	31,82	7,17	3,22	89	72,62	16,37	7,36
40	32,64	7,36	3,30	90	73,44	16,56	7,44
41	33,45	7,54	3,39	91	74,25	16,74	7,52
42	34,27	7,72	3,47	92	75,07	16,92	7,60
43	35,08	7,91	3,55	93	75,88	17,11	7,69
44	35,90	8,09	3,63	94	76,70	17,29	7,77
45	36,72	8,28	3,72	95	77,52	17,48	7,85
46	37,53	8,46	3,80	96	78,33	17,66	7,93
47	38,35	8,64	3,88	97	79,15	17,84	8,02
48	39,16	8,83	3,96	98	79,96	18,03	8,10
49	39,98	9,01	4,05	99	80,78	18,21	8,18
50	40,80	9,20	4,13	100	81,60	18,40	8,27

Mn_2O_3

%	MnO	»O«	± ΔO	%	MnO	»O«	± ΔO
1	0,89	0,10		51	45,83	5,16	
2	2,69	0,30		52	46,73	5,26	
3	2,69	0,30		53	47,63	5,36	
4	3,59	0,40		54	48,52	5,47	
5	4,49	0,50		55	49,42	5,57	
6	5,39	0,60		56	50,32	5,67	
7	6,29	0,70		57	51,22	5,77	
8	7,18	0,81		58	52,12	5,87	
9	8,08	0,91		59	53,02	5,97	
10	8,98	1,01		60	53,92	6,07	
11	9,88	1,11		61	54,82	6,17	
12	10,78	1,21		62	55,71	6,28	
13	11,68	1,31		63	56,61	6,38	
14	12,58	1,41		64	57,51	6,48	
15	13,48	1,51		65	58,41	6,58	
16	14,37	1,62		66	59,31	6,68	
17	15,27	1,72		67	60,21	6,78	
18	16,17	1,82		68	61,11	6,88	
19	17,07	1,92		69	62,01	6,98	
20	17,97	2,02		70	62,90	7,09	
21	18,87	2,12		71	63,80	7,19	
22	19,77	2,22		72	64,70	7,29	
23	20,67	2,32		73	65,60	7,39	
24	21,56	2,43		74	66,50	7,49	
25	22,46	2,53		75	67,40	7,59	
26	23,36	2,63		76	68,30	7,69	
27	24,26	2,73		77	69,19	7,80	
28	25,16	2,83		78	70.09	7,90	
29	26,06	2,93		79	70,99	8,00	
30	26,96	3,03		80	71,89	8,10	
31	27,85	3,14		81	72,79	8,20	
32	28,75	3,24		82	73,69	8,30	
33	29,65	3,34		83	74,59	8,40	
34	30,55	3,44		84	75,49	8,50	
35	31,45	3,54		85	76,38	8,61	
36	32,35	3,64		86	77,28	8,71	
37	33,25	3,74		87	78,18	8,81	
38	34,15	3,84		88	79,08	8,91	
39	35,04	3,95		89	79,98	9,01	
40	35,94	4,05		90	80,88	9,11	
41	36,84	4,15		91	81,78	9,21	
42	37,74	4,25		92	82,68	9,31	
43	38,64	4,35		93	83,57	9,42	
44	39,54	4,45		94	84,47	9,52	
45	40,44	4,55		95	85,37	9,62	
46	41,34	4,65		96	86,27	9,72	
47	42,23	4,76		97	87,17	9,82	
48	43,13	4,86		98	88,07	9,92	
49	44,03	4,96		99	88,97	10,02	
50	44,93	5,06		100	89,87	10,13	

Mn_3O_4

%	MnO	»O«	$\pm \Delta$O	%	MnO	»O«	$\pm \Delta$O
1	0,93	0,06	0,03	51	47,43	3,56	1,60
2	1,86	0,13	0,06	52	48,36	3,63	1,63
3	2,79	0,20	0,09	53	49,29	3,70	1,66
4	3,72	0,27	0,12	54	50,22	3,77	1,69
5	4,65	0,34	0,15	55	51,15	3,84	1,72
6	5,58	0,41	0,18	56	52,08	3,91	1,75
7	6,51	0,48	0,21	57	53,01	3,98	1,78
8	7,44	0,55	0,25	58	53,94	4,05	1,82
9	8,37	0,62	8,28	59	54,87	4,12	1,85
10	9,30	0,69	0,31	60	55,80	4,19	1,88
11	10,23	0,76	0,34	61	56,73	4,26	1,91
12	11,16	0,83	0,37	62	57,66	4,33	1,94
13	12,09	0,90	0,40	63	58,59	4,40	1,97
14	13,02	0,97	0,43	64	59,52	4,47	2,00
15	13,95	1,04	0,47	65	60,45	4,54	2,04
16	14,88	1,11	0,50	66	61,38	4,61	2,07
17	15,81	1,18	0,53	67	62,31	4,68	2,10
18	16,74	1,25	0,56	68	63,24	4,75	2,13
19	17,67	1,32	0,59	69	64,17	4,82	2,16
20	18,60	1,39	0,62	70	65,10	4,89	2,19
21	19,53	1,46	0,65	71	66,03	4,96	2,22
22	20,46	1,53	0,69	72	66,96	5,03	2,96
23	21,39	1,60	0,72	73	67,89	5,10	2,29
24	22,32	1,67	0,75	74	68,82	5,17	2,32
25	23,25	1,74	0,78	75	69,75	5,24	2,35
26	24,18	1,81	0,81	76	70,68	5,31	2,38
27	25,11	1,88	0,84	77	71,61	5,38	2,41
28	26,04	1,95	0,87	78	72,54	5,45	2,44
29	26,97	2,02	0,91	79	73,47	5,52	2,48
30	27,90	2,09	0,94	80	74,40	5,59	2,51
31	28,83	2,16	0,97	81	75,33	5,66	2,54
32	29,76	2,23	1,00	82	76,26	5,73	2,57
33	30,69	2,30	1,03	83	77,19	5,80	2,60
34	31,62	2,37	1,06	84	78,12	5,87	2,63
35	32,55	2,44	1,09	85	79,05	5,94	2,66
36	33,48	2,51	1,13	86	79,98	6,01	2,70
37	34,41	2,58	1,16	87	80,91	6,08	2,73
38	35,34	2,65	1,19	88	81,84	6,15	2,76
39	36,27	2,72	1,22	89	82,77	6,22	2,79
40	37,20	2,79	1,25	90	83,70	6,29	2,82
41	38,13	2,86	1,28	91	84,63	6,36	2,85
42	39,06	2,93	1,31	92	85,56	6,43	2,88
43	39,99	3,00	1,35	93	86,49	6,50	2,92
44	40,92	3,07	1,38	94	87,42	6,57	2,95
45	41,85	3,14	1,41	95	88,35	6,64	2,98
46	42,78	3,21	1,44	96	89,28	6,71	3,01
47	43,71	3,28	1,47	97	90,21	6,78	3,04
48	44,64	3,35	1,50	98	91,14	6,85	3,07
49	45,57	3,42	1,53	99	92,07	6,92	3,10
50	46,50	3,49	1,57	100	93,01	6,99	3,14

$H_4BaMnMn_8O_{20}$

%	MnO	»O«	± Δ O	%	MnO	»O«	± Δ O
1	0,83	0,16		51	42,48	8,51	
2	1,66	0,33		52	43,32	8,67	
3	2,49	0,50		53	44,15	8,84	
4	3,33	0,66		54	44,98	9,01	
5	4,16	0,83		55	45,82	9,17	
6	4,99	1,00		56	46,65	9,34	
7	5,83	1,16		57	47,48	9,51	
8	6,66	1,33		58	48,31	9,68	
9	7,49	1,50		59	49,15	9,84	
10	8,33	1,66		60	49,98	10,01	
11	9,16	1,83		61	50,81	10,18	
12	9,99	2,00		62	51,65	10,34	
13	10,83	2,16		63	52,48	10,51	
14	11,66	2,33		64	53,31	10,68	
15	12,49	2,50		65	54,15	10,84	
16	13,32	2,67		66	54,98	11,01	
17	14,16	2,83		67	55,81	11,18	
18	14,99	3,00		68	56,65	11,34	
19	15,82	3,17		69	57,48	11,51	
20	16,66	3,33		70	58,31	11,68	
21	17,49	3,50		71	59,15	11,84	
22	18,32	3,67		72	59,98	12,01	
23	19,16	3,83		73	60,81	12,18	
24	19,99	4,00		74	61,64	12,35	
25	20,82	4,17		75	62,48	12,51	
26	21,66	4,33		76	63,31	12,68	
27	22,49	4,50		77	64,14	12,85	
28	23,32	4,67		78	64,98	13,01	
29	24,15	4,84		79	65,81	13,18	
30	24,99	5,00		80	66,64	13,35	
31	25,82	5,17		81	67,48	13,51	
32	26,65	5,34		82	68,31	13,68	
33	27,49	5,50		83	69,14	13,85	
34	28,32	5,67		84	69,98	14,01	
35	29,15	5,84		85	70,81	14,18	
36	29,99	6,00		86	71,64	14,35	
37	30,82	6,17		87	72,47	14,52	
38	31,65	6,34		88	73,31	14,68	
39	32,49	6,50		89	74,14	14,85	
40	33,32	6,67		90	74,97	15,02	
41	34,15	6,84		91	75,81	15,18	
42	34,99	7,00		92	76,64	15,35	
43	35,82	7,17		93	77,47	15,52	
44	36,65	7,34		94	78,31	15,68	
45	37,48	7,51		95	79,14	15,85	
46	38,32	7,67		96	79,97	16,02	
47	39,15	7,84		97	80,81	16,18	
48	39,98	8,01		98	81,64	16,35	
49	40,82	8,17		99	82,47	16,52	
50	41,65	8,34		100	83,31	16,69	